

## STUDIES ON TRANSYLVANIAN NATIVE GOLD SAMPLES FROM ROSIA MONTANA AND CAVNIC DEPOSITS USING MICRO-PIXE

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**Abstract** Twenty small samples of Transylvanian native gold from Rosia Montana (Apuseni Mountains) and Cavnica (Gutai Mountains) were scanned by micro-Particle Induced X-ray Emission (micro-PIXE) to identify “fingerprints” trace elements – Sb, Te, Hg – and their possible micro-inclusions (micro-areas of different composition from the surrounding material), as a pre-screening selection of the richest areas in such micro-inclusions samples. In a second phase, to identify the “fingerprints” minerals, the samples were investigated using a Scanning Electron Microscope (SEM) from FEI, model Inspect S with an Energy Dispersive X-Ray Spectroscopy (EDAX) unit. The goal of the study was to demonstrate the Transylvanian gold geological provenance for some valuable archaeological artifacts: Dacian spiraled bracelets and Koson-type coins recently – from 1990 - found in Transylvania. We detected micro-inclusions of Sb minerals in five Rosia Montana samples and of Te minerals in four Cavnica samples. We identified in a sample from Rosia Montana (Cetate) a micrometer area ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) rich in Ag and Sb and reduced in Au, Sb/Ag ratio being 1/3.5-4.5, SEM-EDAX analysis confirming the existence of pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ); in other Rosia Montana sample we identified micro-inclusions of Hg – probably native. In a Cavnica (Roata) sample we found a micro-inclusion of a Te-Ag (Au) mineral, the SEM-EDAX analysis confirming the existence of cervelleite ( $\text{Ag}_4\text{TeS}$ ). Due to Dacian ancient primitive metallurgy (gold high melting point was not reached), “fingerprints” inclusions (mainly nano- but also possible isolated micro-inclusions) are preserved in the artifacts – the case of Sb and Te, giving the possibility to use them but also Hg as “fingerprints” for Transylvanian gold. Our studies proved micro-PIXE is an efficient tool for a first stage of identification of micro-areas containing specific gold “fingerprints”, but for their minerals identification it must be coupled to a SEM-EDAX investigation.

**Key words:** native gold, micro-PIXE, SEM-EDAX, Dacian gold artifacts.

### 1. INTRODUCTION

In the last years, using metal detectors, treasure hunters performed illegally excavations in the area of Sarmizegetusa (the ancient Dacian capital – see [1]), finding many Dacian gold artifacts – spiraled bracelets – [1, 2, 3] and Koson-type coins (staters) – [2, 4]. These hoards were illegally exported, but, from 2007, Romanian authorities in collaboration with international specialized organizations recovered a part of them. One of the most efficient method to authenticate and find the provenance of such ancient gold artifacts was to identify trace elements – Sn, Sb, Zn, Bi, Te, PGA (especially Pt, Ir-Os, Pd) – considered as “fingerprints” for a gold geological source [5, 6, 7], ancient metallurgical techniques not being able to remove them. So, in [5] a micro-inclusion of cassiterite (an alluvial tin oxide) was identified using Scanning Electron Microscopy – SEM (tin traces are generally considered an indicator for alluvial gold) in a Chinese gold artifact dated 3<sup>rd</sup> Century BC to 1<sup>st</sup> Century AD. In [7] traces of tin, antimony and nickel were detected in a Central Asia gold belt presumably from 6<sup>th</sup>-3<sup>th</sup> Centuries BC. We also found [2, 3] traces of tin, antimony and tellurium preserved in Dacian gold artifacts, most probably nano-inclusions as a consequence of ancient primitive metallurgy (gold high melting point was not reached), micro-SR-XRF (Synchrotron Radiation – X-Ray Fluorescence) and micro-PIXE (micro Proton Induced X-ray Emission) being adequate investigation tools [3].

Because the artifacts from Romanian museums most probably have as gold source the Transylvanian mountains, to explain the presence of these nano (micro)-inclusions in Dacian artifacts it was necessary to identify them (including as “fingerprints” minerals) in native gold from this region. Our study was conducted on electrum (native gold) samples from Rosia Montana - Cetate Quarry (Pit), Apuseni Mountains - a famous gold mine exploited even from Roman times (2<sup>nd</sup> Century AD) and from Cavnic deposit – Roata mine, Gutai Mountains (north-west of Transylvania) [8], having a long history of mining, probably beginning in Roman times, but the most intense exploitation occurred during the last 60 years [9].

We used micro-PIXE at AN2000 accelerator of Laboratori Nazionali di Legnaro (LNL), INFN, Italy [10], to obtain information on gold and silver minerals, e.g. antimony and tellurium compounds, Sb and Te being well known “fingerprints” for the Transylvanian gold sources as discussed in [4]. The elemental maps for Ag, Sb, and Te obtained by micro-PIXE were used as a pre-screening to select the richest in Ag-Sb and Ag-Te minerals samples.

In a second phase, to identify the minerals (their chemical formula), after a special preparation (embedding in a resin and polishing with diamond powder) and a short investigation using a polarized light microscope to see the most relevant micro-areas with Sb and Te minerals, the samples were studied using a Scanning Electron Microscope (SEM) from FEI, model Inspect S with an Energy Dispersive X-Ray Spectroscopy (EDAX) unit obtaining the stoichiometrical information. In this way, a secondary goal of our study was to demonstrate the importance of micro-PIXE for a first selection of native gold samples having Sb and Te minerals as micro-inclusions.

## 2. EXPERIMENTAL

### 2.1. The Set-ups

To identify “fingerprints” elements and their possible micro-inclusions’ “topography” (micro-areas of different composition from the surrounding material – e.g. in our case rich in antimony and tellurium), we scanned the samples using micro-PIXE, preserving the samples as they were. We used a 2 MeV proton micro-beam ( $6\ \mu\text{m} \times 6\ \mu\text{m}$  spot size) with a maximum beam current  $\sim 1000\ \text{pA}$  [11, 12]. The characteristic X-rays were measured with a Canberra HPGe detector (180 eV FWHM at 5.9 keV). An Al funny filter (80  $\mu\text{m}$  thick and 8% hole) in front of the X-ray detector was used to reduce the intensity of the peaks in the low spectral region (below 4 keV).  $2\ \text{mm} \times 2\ \text{mm}$  maps and point spectra were acquired. The quantitative analysis was performed using the GUPIXWIN software [13].

For a definitely mineralogical identification, we continued with a SEM-EDAX investigation at an FEI microscope, working in both low and high vacuum, acceleration voltage up to 30 kV. The EDAX unit has a Si (Li) detector and is powered by EDAX Genesis Software [14]. For our measurements we used a ZAF ( $Z$  = the atomic number,  $A$  = absorption correction,  $F$  = fluorescence correction) standard-less quantification procedure, with background subtraction, matrix correction and normalization to 100%. The usual results are within 1% error range, slightly higher for light elements.

### 2.2. The Samples

The analyzed samples are from recoveries obtained by Rosia Montana inhabitants from existing on-site landfills of the former Cetate hill exploited in quarry mode during 1970-1990 – ten samples, and by Cavnic people from Roata mine abandoned in 2005 – ten samples.

## 3. RESULTS AND DISCUSSION

For Rosia Montana (Cetate) samples, we focused on the existence of areas rich in silver and antimony (gold having a reduced presence), finding them in five samples. The most relevant is Sample no. 2 – see Au, Ag, Sb maps from Fig. 1.

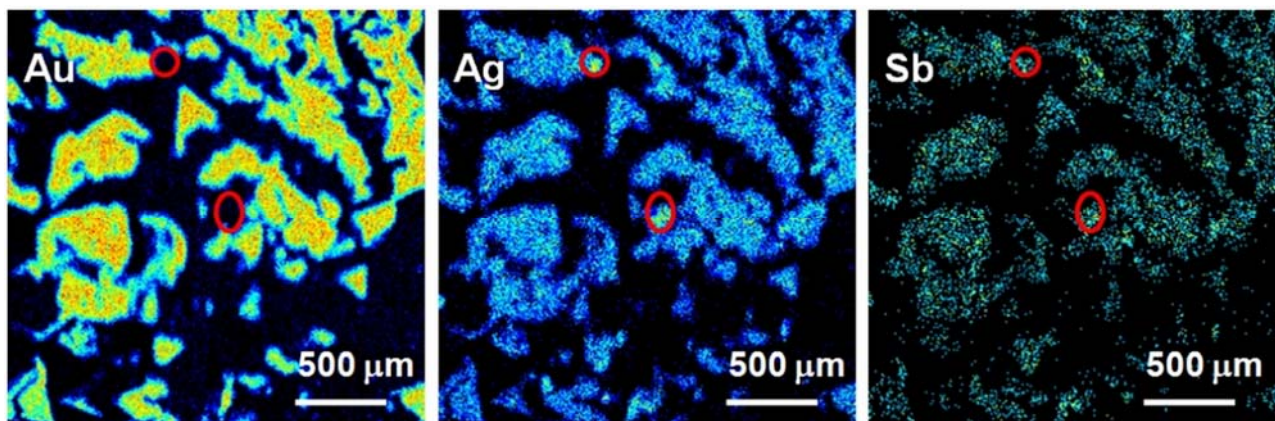


Fig. 1 – Micro-PIXE elemental maps; Rosia Montana (Cetate)  
Sample no. 2 (AN2000 microprobe).

The point spectra in the marked areas from Fig. 1 (red circles) revealed the possible existence of Sb-Ag minerals. Such a point ( $5\ \mu\text{m} \times 5\ \mu\text{m}$  area) spectrum in the central silver area without a relevant gold presence (but with arsenopyrite –  $\text{FeAsS}$ ) is represented in Fig. 2. Sb/Ag peaks ratio is approx. 1/4, indicating from the stoichiometric point of view the existence of stephanite ( $\text{Ag}_5\text{SbS}_4$ ) or pyrargyrite ( $\text{Ag}_3\text{SbS}_3$ ). The GUPIXWIN program gave for this “point” the following concentrations (% weight):  $\text{Au} = 2.17\%$ ,  $\text{Ag} = 39.69\%$ ,  $\text{Sb} = 11.45\%$  confirming silver compounds domination. Unfortunately, due to the interference of  $\text{AuM-SK}$  rays it is not possible to correctly evaluate sulfur concentration.

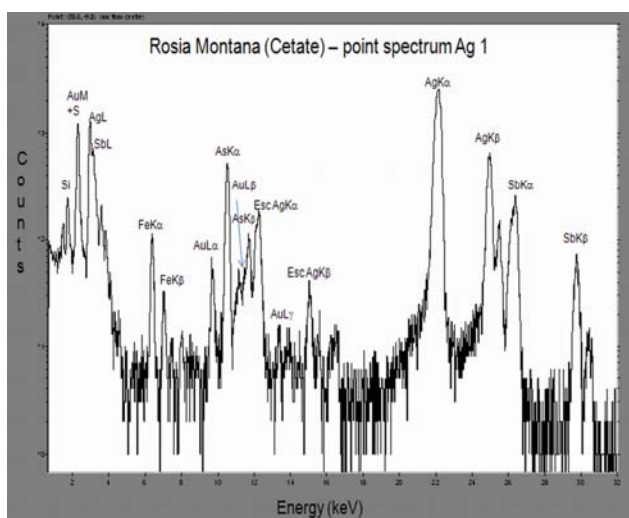


Fig. 2 – Micro-PIXE point spectrum; Rosia Montana (Cetate)  
Sample no. 2, Sb + Ag mineral (AN2000 microprobe).

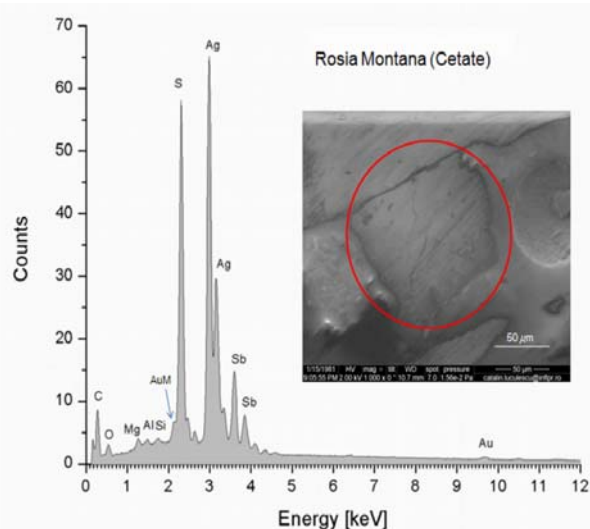


Fig. 3 – SEM image and EDAX spectrum; Rosia Montana (Cetate)  
Sample no. 2, Sb + Ag mineral (pyrargyrite).

To definitely confirm the presence of stephanite or pyrargyrite, we examined Sample no. 2 using SEM - EDAX (see Fig. 3), obtaining the spectrum and the chemical composition from Table 1 (C and O are remnants of the polishing agent). The atomic ratios  $\text{Ag/Sb/S}$ : 16.28/4.51/15.42 indicated pyrargyrite –  $\text{Ag}_3\text{SbS}_3$  (in this case  $\text{AuM-SK}$  rays are well separated). The existence of such Sb minerals micro-inclusions in Transylvanian native gold explains the Sb traces found in some Dacian gold artifacts, most probably as nano-inclusions preserved by a primitive metallurgy – see [2 nano-inclusions preserved by a primitive metallurgy – see [2].

Table 1

The chemical composition of Rosia Montana (Cetate)  
Sample no. 2 resulting from EDAX analysis

Element	X-Ray Line	Weight %	Atomic %
C	K $\alpha$	17.55	54.22
O	K $\alpha$	3.18	7.37
Mg	K $\alpha$	0.62	0.95
Al	K $\alpha$	0.3	0.42
Si	K $\alpha$	0.25	0.33
S	K $\alpha$	13.32	15.42
Ag	L $\alpha$	47.33	16.28
Sb	L $\alpha$	14.8	4.51
Au	L $\alpha$	2.65	0.5
Total		100	100

An interesting result was the presence of Hg in some point spectra from Sample no. 5 – see Fig. 4.

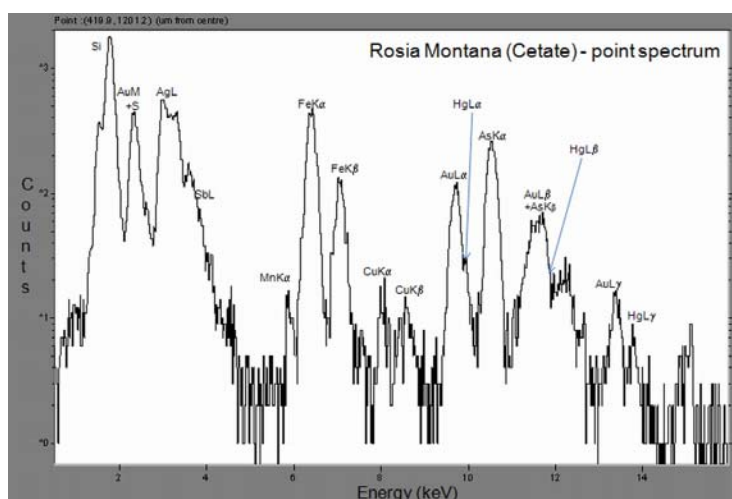


Fig. 4 – Micro-PIXE point spectrum; Rosia Montana (Cetate)  
Sample no. 5, Hg presence (AN2000 microprobe).

A confirmation of (probably) native metal Hg presence in this sample was subsequently obtained using the new multi-detector and systematic imaging system on the AGLAE accelerator external beam [15]. We detected in this sample an important Hg presence – see Au, Ag, Hg maps (700  $\mu\text{m} \times 500 \mu\text{m}$ ) in Fig. 5.

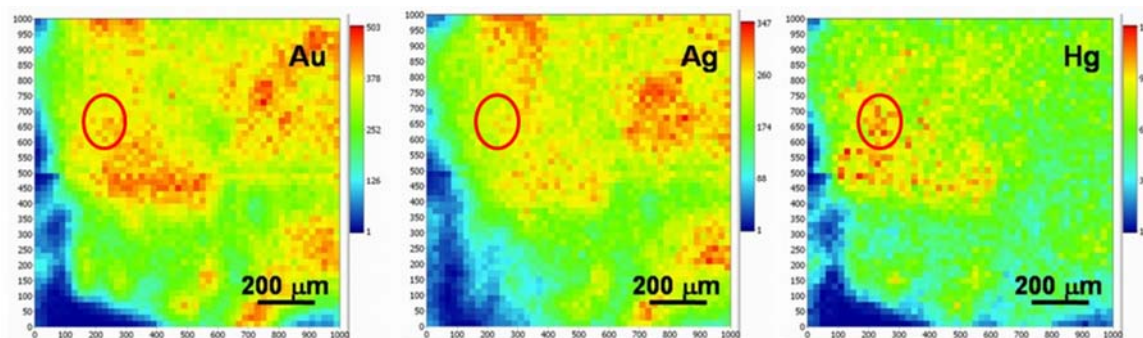


Fig. 5 – Micro-PIXE elemental maps; Rosia Montana (Cetate) Sample no. 5, Hg presence (AGLAE microprobe).

The GUPIXWIN program gave for one “point” - small area of  $20\ \mu\text{m} \times 20\ \mu\text{m}$  – in the marked area (red circle) the following concentrations: Au = 24.34%, Ag = 3.98%, Cu = 0.83%, Hg = 21.74% (Au, Ag, Cu are the components of the native gold alloy). Most probably Hg is present as native metal (S presence can't be estimated due to the interference of AuM-SK rays). Thus, Hg micro-inclusions could also be used as “fingerprints” for Transylvanian native gold in the authentication process of Dacian gold artifacts.

For Căvnic (Roata) samples we focused on the existence of areas rich in silver and tellurium, gold having a more reduced presence, finding them in four samples. The most relevant is Sample no. 5 – see Au, Ag, Fe, As maps from Fig. 6, where a strong presence of arsenopyrite (FeAsS) was also identified. Point spectra in the marked area from Fig. 6 (red circle) revealed the possible existence of Te-Ag (Au) minerals – see Fig. 7.

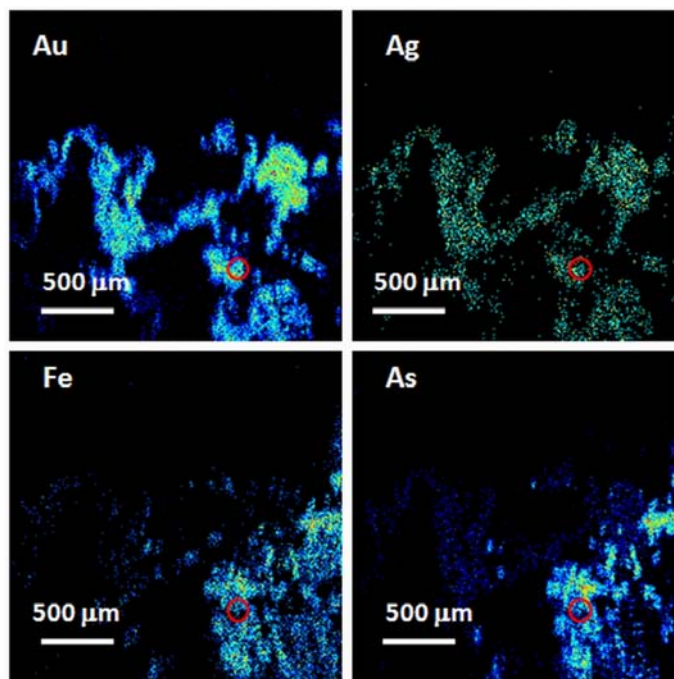


Fig. 6 – Micro-PIXE elemental maps; Cavnic (Roata) Sample no. 5 (AN2000 microprobe).

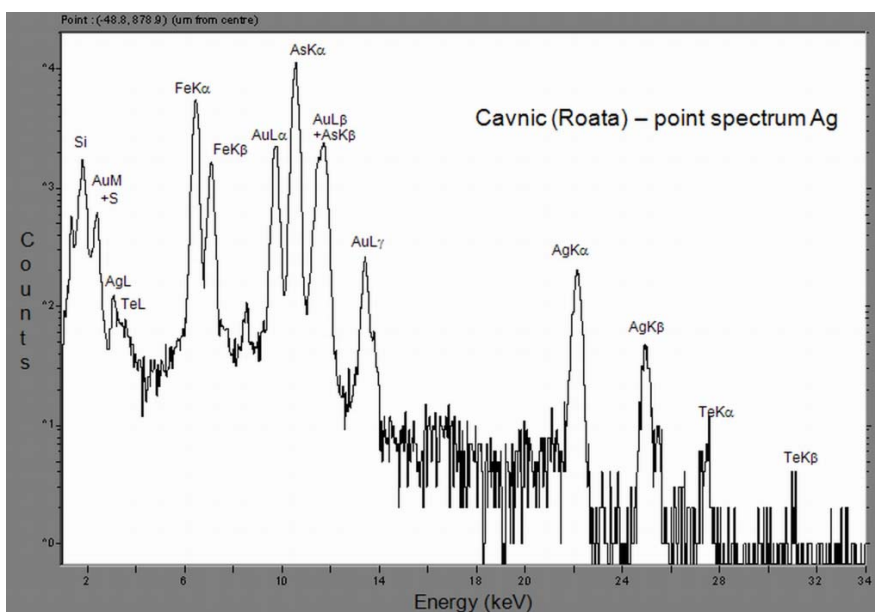


Fig. 7 – Micro-PIXE point spectrum; Cavnic (Roata) Sample no. 5, Ag + Te mineral (AN2000 microprobe).



To identify the Te-Ag(Au) mineral, we examined Sample no. 5 using SEM - EDAX (see Fig. 8), obtaining the spectrum and the chemical composition from Table 2 (C and O are remnants of the polishing agent). The ratios Ag/Te/S: 15.05/4.02/4.43 indicated cervelleite –  $\text{Ag}_4\text{TeS}$ . The existence of such Te minerals micro-inclusions in Transylvanian native gold offers the possibility to use Te also as “fingerprint” for authentication of Dacian gold artifacts.

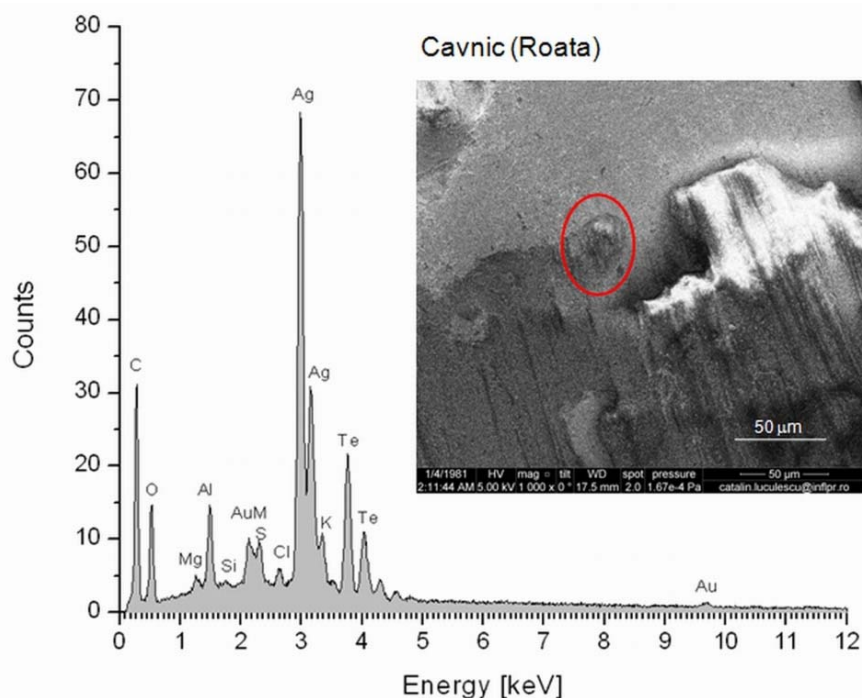


Fig. 8 – SEM image and EDAX spectrum; Cavnic (Roata)  
Sample no. 5, Ag + Te mineral (cervelleite).

Table 2

The chemical composition of Cavnic (Roata)  
Sample no. 5 resulting from EDAX analysis

Element	X-Ray Line	Weight %	Atomic %
C	K $\alpha$	23.36	52.61
O	K $\alpha$	9.22	17.67
Mg	K $\alpha$	0.86	1.08
Al	K $\alpha$	2.72	3.1
Si	K $\alpha$	0.49	0.53
S	K $\alpha$	1.5	4.43
Cl	K $\alpha$	0.33	0.29
Ag	L $\alpha$	38.87	15.05
K	K $\alpha$	0.36	0.28
Sn	L $\alpha$	0.7	0.18
Te	L $\alpha$	16.71	4.02
Au	L $\alpha$	4.88	0.76
Total		100	100

#### 4. CONCLUSIONS

We demonstrated the existence of Sb, Hg, and Te minerals micro-inclusions in Transylvanian native gold which explains the presence of Sb traces in Dacian gold artifacts (most probably as nano-inclusions, but their identification in such precious artifacts is extremely difficult) due to the primitive metallurgy and gives the possibility to use Hg and Te also as “fingerprints” for this gold. Our studies proved that micro-PIXE is an efficient tool for a first stage of identification of micro-areas containing specific gold “fingerprints”, but for their minerals identification it must be coupled to a SEM-EDAX investigation.

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